

OFFICE OF NAVAL RESEARCH

GRANT: N00014-93-1-0375-1

R&T Code 3133043
Robert Nowak

Pulse Voltammetric Characterization of Biocorrosion Processes

by

Janet G. Osteryoung

North Carolina State University
Department of Chemistry
Raleigh, NC 27695-8204

February 21, 1997

Reproduction in whole or in part is permitted for any purpose of the United States
Government.

This document has been approved for public release and sale; its distribution is unlimited.

19970303 098

REPORT DOCUMENTATION PAGE

*Form Approved
OMB No. 0704-0188*

Public reporting burden for this collection of information is estimated to average 1 hour per response, including the time for reviewing instructions, searching existing data sources, gathering and maintaining the data needed, and completing and reviewing the collection of information. Send comments regarding this burden estimate or any other aspect of this collection of information, including suggestions for reducing this burden, to Washington Headquarters Services, Directorate for Information Operations and Reports, 1215 Jefferson Davis Highway, Suite 1204, Arlington, VA 22202-4302, and to the Office of Management and Budget, Paperwork Reduction Project (0704-0188), Washington, DC 20503.

1. AGENCY USE ONLY (Leave blank)			2. REPORT DATE			3. REPORT TYPE AND DATES COVERED		
						Final Report 2/1/93 - 7/31/96		
4. TITLE AND SUBTITLE Pulse Voltammetric Characterization of Biocorrosion Processes						5. FUNDING NUMBERS Grant: N00014-93-1-0375-1 RAT: 3133043		
6. AUTHOR(S) Janet G. Osteryoung								
7. PERFORMING ORGANIZATION NAME(S) AND ADDRESS(ES) NCSU						8. PERFORMING ORGANIZATION REPORT NUMBER		
9. SPONSORING/MONITORING AGENCY NAME(S) AND ADDRESS(ES) ONR						10. SPONSORING/MONITORING AGENCY REPORT NUMBER		
11. SUPPLEMENTARY NOTES								
12a. DISTRIBUTION/AVAILABILITY STATEMENT						12b. DISTRIBUTION CODE		
13. ABSTRACT (Maximum 200 words) The work on anodization of copper electrodes for the first time presented a closed-form solution to the problem of relating the distribution of products of metal oxidation to the potential of the metal. In addition it presented a new method, based on normal pulse voltammetry at microelectrodes, for the determination of the stability constants of complexes, especially appropriate for the formation of chloride complexes in seawater. This work also identified and treated qualitatively the problem of coupled migration, diffusion, and complex formation in seawater. The work on thermoconvection provided a quantitative treatment of the effect of temperature differences on the rate of metal dissolution or deposition. Enhanced rates due to thermoconvection are observed for both negative and positive gradients, and the gradient has a strong qualitative influence on the potential dependence of the current. Thermal gradients are common in copper-containing equipment in contact with seawater. This work explains the consequence of such gradients.								
14. SUBJECT TERMS corrosion, copper, thermoconvection, complex formation, normal pulse voltammetry						15. NUMBER OF PAGES		
						16. PRICE CODE		
17. SECURITY CLASSIFICATION OF REPORT unclassified			18. SECURITY CLASSIFICATION OF THIS PAGE unclassified			19. SECURITY CLASSIFICATION OF ABSTRACT unclassified		
20. LIMITATION OF ABSTRACT								

**OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT**

R&T Number: 3133043
Contract/Grant Number: N00014-93-1-0375-1
Contract/Grant Title: Pulse Voltammetric Characterization of Biocorrosion Processes
Principal Investigator: Janet G. Osteryoung
Mailing Address: North Carolina State University, Office of Sponsored Programs,
Box 7514, Raleigh, NC 27695-7514

Phone Number: (919) 515 6446

Fax Number: (919) 515 5486

E-mail Address: chejgo@chemdept.chem.ncsu.edu

WWW Homepage: <http://www2.ncsu.edu/ncsu/chemistry/chem.html>

- a. Number of papers submitted to refereed journals, but not published: 0
- b. + Number of papers published in refereed journals (for each, provide a complete citation): 2
- c. + Number of books or chapters submitted, but not yet published: 0
- d. + Number of books or chapters published (for each, provide a complete citation): 0
- e. + Number of printed technical reports/non-refereed papers 0
(for each, provide a complete citation): 0
- f. Number of patents filed: 0
- g. + Number of patents granted (for each, provide a complete citation): 0
- h. + Number of invited presentations (for each, provide a complete citation): 17
- i. + Number of submitted presentations (for each, provide a complete citation): 5
- j. + Honors/Awards/Prizes for contract/grant employees (list attached): 9

(This might include Scientific Society Awards/Offices, Selection as Editors,
Promotions, Faculty Awards/Offices, etc.)

- k. Total number of Full-time equivalent Graduate Students and Post-Doctoral associates supported
during this period, under this R&T project number: 4.55

Graduate Students: 0.9

Post-Doctoral Associates: 3.4

including the number of:

Female Graduate Students: .25

Female Post-Doctoral Associates: 0

the number of:

Minority* Graduate Students: 0

Minority* Post-Doctoral Associates: 0

and the number of:

Asian Graduate Students: 0

Asian Post-Doctoral Associates: 0

- l. Other funding (list agency, grant title, amount received this year, total amount, period of performance
and a brief statement regarding the relationship of that research to your ONR grant)

+ Use the letter and an appropriate title as a heading for your list, e.g.:

- b. Published Papers in Refereed Journals; or
- d. Books and Chapters published.

Submit the citation lists as ASCII files via e-mail or via PC-compatible floppy disks

* Minorities include Blacks, Aleuts, AmIndians, Hispanics, etc. NB: Asians are not considered an
under-represented or minority group in science and engineering.

**OFFICE OF NAVAL RESEARCH
PUBLICATIONS/PATENTS/PRESENTATIONS/HONORS REPORT**

a. Number of Papers Published: 2

Anodization of Copper Microelectrodes in a Complexing Medium. Determination of Stability Constants of Products, Orr, James T., Osteryoung, Janet G., Analytical Chemistry 67, 2714-2722 (1995).

Thermoconvection-Enhanced Deposition of Copper, Isaev, N., and Osteryoung, Janet G., Journal of the Electrochemical Society 142, 4103-4107 (1995)

h. Number of Invited Presentations: 17

From Azobenzene to Zinc, Tennessee Tech Chapter-Sigma Xi, Cookeville, TN, October 1993.

Electroanalytical Chemistry of the Environment, Department of Chemistry, Tennessee Tech, Cookeville, TN, October 1993.

Modern Voltammetry, Kansas City Section, Kansas City, MO

Modern Voltammetry, Southeast Kansas City Section, Pittsburgh State University, Pittsburgh, KS

Modern Voltammetry, Wichita Section, Wichita, KS

Women in Analytical Chemistry, 76th Canadian Society for Chemistry Conference, Sherbrooke, Quebec, Canada, June 1993

Pulse Voltammetry, Seventh National Conference on Analytical Chemistry, Rio de Janeiro, Brazil, September 1993

Applications of Square Wave Voltammetry, Department of Chemistry, University of South Carolina, October 1993

Modern Voltammetry, Kansas State University Section, Kansas State University, Manhattan, KS

Electrochemistry: Current and Future, Roche Carolina Symposium, Francis Marion University, Florence, SC, May 1994

Electroanalytical Chemistry of the Environment, Spelman College, Atlanta, GA, July 1994.

Mechanisms and Analytical Applications of Surface Processes at Electrodes,
Georgetown University, Washington, DC, September 1994.

Square-Wave Voltammetry for Studies of Mechanism, W. Virginia University,
Morgantown, WV, September 1994.

Modern Electroanalytical Chemistry, 45th Annual Meeting of the International
Society of Electrochemistry, Porto, Portugal, September 1994.

Square-Wave Voltammetry, U. of Wisconsin at Milwaukee, Milwaukee, WI,
October 1994.

Modern Electroanalytical Chemistry, The Mississippi Chemical Company
Lectureship, University of Mississippi, Oxford, MS, October 1994.

Analytical Applications of Pulse Voltammetry, American Chemical Society,
Washington Capitol Section, Washington, DC, November 1994.

i. Number of Submitted Presentations: 5

Computational and Experimental Aspects of Copper Anodization, NC ACS
Sectional Conference, NCSU, April 1994 (with J. T. Orr)

Thermoconvection-Enhanced Deposition-Dissolution of Copper, 185th
Electrochemical Society Meetg, San Francisco, May 1994 (with Nick Isaev)

Anodic Reactions of Copper; poster, 45th Annual Meeting of the International
Society of Electrochemistry, Porto, Portugal, September 1994 (with J. T. Orr and
K. Wikiel).

Determination of Formation Constants of Products of Copper Anodization, 186th
Meeting of The Electrochemical Society, Miami Beach, FL, October 1994 (with J.
T. Orr and K. Wikiel).

Interdigitated Array Electrode Sensor for Copper Species, 109th Sectional
Conference, North Carolina Section, American Chemical Society, Chapel Hill, NC,
April 1995 (with J. Urbanik).

j. Honors/Awards/Prizes (J. Osteryoung): 10

Chair-elect and Program Chair, Analytical Division, ACS, 10/1992-9/1993

Scientific Advisory Council, National Institute of Statistical Sciences, 1993-

Chair, Analytical Division, ACS, 10/1993-9/1994

Director, Chemistry Division, National Science Foundation, 1994

Immediate Past-Chair, Analytical Division, ACS, 10/1994-9/1995.

Participant, Electrochemical Sciences Program Review, Office of Naval Research, January, 1995.

Vice-Chair, Gordon Research Conference on Electrochemistry, January 1995.

Program Committee, Council on Chemical Research, 1994-1995.

Chair, Gordon Research Conference on Electrochemistry, 1996.

American Chemical Society Analytical Division Award in Electrochemistry, August, 1996.

1. Other Support:

Agency, Grant Title	Amt. This Year \$k	Total Amount \$k	Period
ARPA, Technology Reinvestment Program	175,000	349,203	8/15/94-12/31/96

This project involves advanced plating systems. In the course of these studies, we have considered systems in which migration and homogeneous equilibria are involved, which makes them formally equivalent to the problem of anodization of copper in seawater.

NSF, Analytical Pulse Voltammetry	102,000	389,000	3/1/92-2/28/97
-----------------------------------	---------	---------	----------------

The two main topics are studies of transport in polyelectrolyte and other systems by voltammetry at microelectrodes and the analytical chemistry and reduction mechanisms of adsorbates on mercury electrodes. Neither of these projects is directly related to the ONR grant, but both provide fundamental results which support the ONR-funded work. In particular, we are gaining valuable experience with polyelectrolytes and are exploring the problem of coupled migration and homogeneous equilibria.

NSF, U.S. Poland Cooperation in Analytical Pulse Voltammetry	11,000	32,300	9/1/92- 1/31/96
---	--------	--------	--------------------

This grant supports travel and visiting scientists for collaboration with Z. Stojek of the University of Warsaw on the main NSF grant.

NSF, Visiting Committee to Poland	26,328	39,505	3/1/94- 8/31/95
--------------------------------------	--------	--------	--------------------

This grant supports assessment of chemical research in Poland through a visit and subsequent report.

Importance of Publications:

The work on anodization of copper electrodes for the first time presented a closed-form solution to the problem of relating the distribution of products of metal oxidation to the potential of the metal. In addition it presented a new method, based on normal pulse voltammetry at microelectrodes, for the determination of the stability constants of complexes, especially appropriate for the formation of chloride complexes in seawater. This work also identified and treated qualitatively the problem of coupled migration, diffusion, and complex formation in seawater. Most studies of corrosion products are qualitative. This lengthy paper lays the foundation for quantitative studies.

The work on thermoconvection provided a quantitative treatment of the effect of temperature differences on the rate of metal dissolution or deposition. Enhanced rates due to thermoconvection are observed for both negative and positive gradients, and the gradient has a strong qualitative influence on the potential dependence of the current. Thermal gradients are common in copper-containing equipment in contact with seawater. This work explains the consequence of such gradients.

Importance of Award:

The Award for Electrochemistry of the Analytical Division of the ACS signifies the general regard in which the above work is held.